The Evaluation of Combustion Mechanisms Using Local and Global Sensitivity and Uncertainty Methods

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The use of computational modelling as a design tool is increasing within engineering applications. Models can often reduce the burden of expensive experimental programmes within the design process and can be used to explore situations and parameter regions that cannot be reached by experiment. One area of particular importance is that of combustion reactor design. Ever more stringent environmental legislation means that engineers are faced with the challenge of developing combustion applications with lower and lower emissions of pollutants such as nitrogen and sulphur oxides. The range of fuel types used for energy generation may also become broader in the future as biomass fuels increase their market share. Understanding the impact of fuel trace elements such as nitrogen and sulphur containing compounds on pollutant emissions is therefore important and requires the inclusion of complex chemical mechanisms describing the interaction between large numbers of species within the combustion chamber.

In many cases the input parameters to the chemical mechanism such as rate constants and thermo-chemical parameters are very poorly categorised. For some well known systems such as, for example, methane (natural gas) combustion, elementary reaction rates used in the chemical mechanism have been extensively measured experimentally and evaluated rate data has been published for the majority of important reactions. For other fuels the elementary pathways are less well understood and significant uncertainties exist in the mechanisms describing complex fuels such as kerosene or biomass fuels. For many processes likely pathways are being determined but the determination of chemical rate data for these elementary reactions is a time-consuming process and is not progressing at the same rate. The net result is that within process engineering applications, chemical kinetic models are potentially becoming more detailed and therefore bigger, but much of the associated rate data is either uncertain due to few measurements and evaluations, or has to be estimated. If confidence is to be placed in the design process then the uncertainty in output predictions resulting from the use of such complex mechanisms should be investigated. For reactions with a high sensitivity these uncertainties may propagate through to the outputs leading to large variations in the predicted concentrations of important pollutants.

Local/linear sensitivity analysis techniques have been used extensively in the past to evaluate such mechanisms. They have been developed in a generic way for use by a large number of researchers in the chemical/process engineering field using packages such as CHEMKIN (Kee et al., 1991) and KINAL (Turanyi,1990). They are employed because they are computationally efficient, but present significant problems for situations where uncertainties in inputs are large and models are highly non-linear. This work therefore describes the development of methods for global sensitivity and uncertainty analysis for application within generic modelling packages such as CHEMKIN. CHEMKIN is used by a large part of the process engineering

community for a range of applications such as chemical mechanism development and validation in simplified flow environments such as continuously stirred tank reactors, 1 dimensional and counter flow diffusion flames.

The paper will present a comparison of local and global methods used for a test case describing a 1 dimensional model of the influence of sulphur containing species on the emission of NO from low pressure methane air flames of various stoichiometries. Experiments show that the influence of sulphur within the flame can lead to both enhancement and reduction of NO emissions depending on whether the flame is fuel rich or fuel lean. The model represents coupled reaction and diffusion driven transport processes for a large number of chemical species, where the coupling between the species is governed by the chemical reactions taking place. The chemical mechanism employed has been developed using evaluated rate data where possible with very little optimisation of rate parameters. It contains 339 reversible reactions representing the chemical interactions between carbon, hydrogen, oxygen and nitrogen containing species, and 153 reversible reactions representing reactions of sulphur containing species. The model therefore consists of a large number of coupled partial differential equations which are not trivial to solve numerically. Predictions from the model have been evaluated over comprehensive target experimental data sets for a variety of flames and fuel nitrogen contents. Without sulphur present in the fuel the model shows good agreement with experimental profiles of key species. However, when sulphur is present, the model is shown to be rather poor at capturing the quantitative influence of sulphur in the flame on NOx emissions which is demonstrated in the 1D flame experiments (Hughes et al. 2001).

Local sensitivity analysis has already revealed (Hughes et al. 2001) several important reactions that require improved categorisation of the rate data to lower output variance. However, the application of global screening methods such as the Morris One at a Time (MOAT) methods reveal strong non-linear interactions between some of the input parameters with respect to their impact on the output variance of NO emission. The results will demonstrate that the Morris method reveals several important but highly non-linear parameters who's importance cannot easily be detected using standard Monte Carlo methods coupled with scatter plot analysis. In particular, some parameters are revealed to have NO sensitivities which change sign within different regions of the input parameter space. The Morris method also shows that very few of the 153 input reaction parameters have a strong effect on the output, allowing a full Monte Carlo analysis to be carried out with far fewer runs than would theoretically be estimated to be necessary. The full Monte Carlo analysis highlights the importance of several key reactions, some of which have a linear response and were also highlighted by the local sensitivity analysis. Other parameters show non-linear regions and sensitivities that saturate in some regions of the input space.

The combined use of Morris and Monte Carlo methods reveals that for fuel rich flames the experimental observations can only be reproduced by the model if values of several of the important parameters are selected from the extremes of their input ranges. For the fuel lean flame the experimental results are not observable using any values of the input parameters. This provides useful information relating to the model structure and suggests that several important reaction steps may be missing from the mechanism. Possible key steps could in the future be revealed by the future application of automatic mechanism generation techniques coupled with global uncertainty methods.

The final part of the paper will address the use of reduced model representations for the development of efficient methods for Monte Carlo Analysis. In this case the use of fitted orthonormal polynomials (Lowe and Tomlin, 2000) to represent input output relationships will be demonstrated for the flame example. The efficiency and accuracy of this method when compared to statistics obtained from a full Monte Carlo analysis of detailed flame model will be shown.

References:

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